



Molybdenum-doped carbon nitride as an efficient heterogeneous catalyst for direct amination of nitroarenes with arylboronic acids

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ABSTRACT

Heterogeneous metal-catalyzed chemical conversions with a recyclable catalyst are very ideal and challenging for sustainable organic synthesis. A new bipyridyl-Mo(IV)-carbon nitride (CN-K/Mo-Bpy) was prepared by supporting molybdenum complex on C₃N₄-K and characterized by FT-IR, XRD, SEM, XPS and ICP-OES. Heterogeneous CN-Mo-Bpy catalyst can be applied to the direct amination of nitroarenes and arylboronic acid, thus constructing various valuable diarylamines in high to excellent yields with a wide substrate scope and good functional group tolerance. It is worth noting that this heterogeneous catalyst has high chemical stability and can be recycled for at least five times without reducing its activity.

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Amine as raw material is one of the fastest growing sectors in the global chemical and pharmaceutical industries. Among them, diarylamine is the most important structural unit in various natural products and drug molecules, such as tolfenamic acid (A) with antibacterial activity, mefenamic acid (B) with antibacterial activity [1], SIRT1 inhibitor (C) [2], antifungal agent (D) [3], KSP inhibitor (E) [4], Bosutinib (F) as an orally active Src and Abl kinase inhibitor [5], cytotoxic antitumor agent (G) [6], and Rilpivirine (H) as a new non-nucleoside reverse transcriptase inhibitor [7] (Fig. 1). They are also widely used in the fields of agrochemical industries, dyes, electronic industries and functional materials. Accordingly, synthetic approaches for diarylamines have received increasing attention. Traditionally, the strategies for the preparation of diarylamines include Buchwald–Hartwig amination of aryl halides [8], Ullmann type C–N cross-coupling reaction [9], Chan–Lam–Evans couplings [10], and reductive amination [11]. These amination processes employ aryl amines as nitrogen sources, which are usually prepared by reducing nitroarenes. Compared with aryl amines, the direct use of nitroarene as the coupling partner not only improves the economy of steps and saves time, but also allows tolerance to unprotected amines. Consequently, there are some reports about the synthesis of diarylamine from nitroaromatic compounds.

In 2002, the group of Knochel first reported a two-step sequential preparation of diarylamines by addition and reduction of arylmagnesium compounds with nitroaromatic hydrocarbons (Scheme 1a) [12]. In 2021, Xue's research group reported the direct amination of aryl halides with nitroaromatics catalyzed by Ni(II)-aryl complexes with *N,N*-diisopropylethylamine (DIPEA) as organic base under purple light irradiation (Scheme 1b) [13]. Lately, Weix *et al.* reported the palladium-catalyzed reductive arylation of nitroaromatics with chloroarenes [14]. Boronic acids are stable, cost-effective, versatile, easily obtained from commercial sources or easily synthesized raw chemical materials, which shows a wide range of functional group compatibility and synthesis diversity, and they are expansively applied in medicine, biology, organic synthesis, industry of fine chemicals and materials production [15]. In 2018, the group of Luzung and Radosevich demonstrated that nitro compounds could serve as a nitrogen source for direct amination of arylboronic acid by using organophosphorus as a catalyst and phenylsilane as reducing agent (Scheme 1c) [16]. Almost simultaneously, the group of Suárez-Pantiga and Sanz reported direct amination of nitro compounds could be achieved with boronic acids by the combination of triphenylphosphine as a cheap reducing agent and molybdenum(VI) dioxide as a catalyst [17]. In 2021, Driver *et al.* improved this reaction by using Cu(OAc)₂ as catalyst, diphosphine (DPPB) as the ligand and phenylsilane as stoichiometric terminal reducing agent at 60 °C [18]. Song's group designed nanoporous MoO₃ confined in silica (MoO₃@m-SiO₂) catalyst and it exhibited improved catalytic performance for this reaction in

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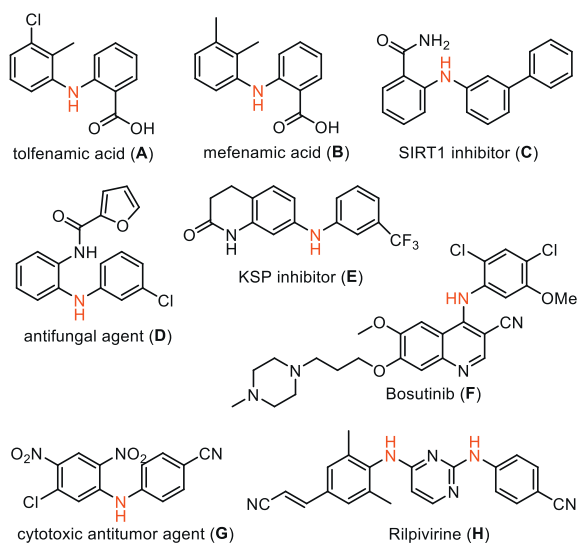
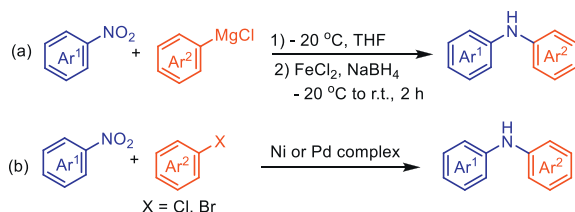
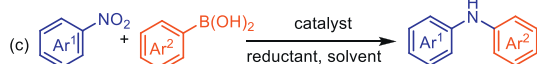


Fig. 1. Typical diarylamines found in natural and bioactive compounds.



Ref. 13: Ni complex (10 mol%), 390 - 395 nm LEDs, DIPEA (3.0 equiv.), toluene, 70°C , 12 h

Ref. 14: $\text{Pd}(\text{OAc})_2$ (5 mol%), BrettPhos (5 mol%), HFIP (1.75 equiv.), Mn (8.0 equiv.), DMF, 100°C , 16 h



Previous works:

Ref. 16: P(III)/PV=O (15 mol%), PhSiH_3 (2.0 equiv.), *m*-xylene, 120°C , 2-24 h

Ref. 17: $\text{MoO}_2\text{Cl}_2(\text{dmf})_2/\text{bpy}$, PPh_3 (2.4 equiv.), toluene, 100°C , 24 h

Ref. 18: $\text{Cu}(\text{OAc})_2$, DPPB, PhSiH_3 (2.8 equiv.), MeCN/PhMe, 60°C , 30 h

Ref. 19: $\text{MoO}_3@m\text{-SiO}_2$, PPh_3 (3.0 equiv.), toluene, N_2 , 100°C , 24 h

Ref. 20: $\alpha\text{-MoO}_3\text{-B}$, PPh_3 (3.0 equiv.), toluene, N_2 , 365 nm LEDs, 24 h

Ref. 21: $\text{W}(\text{CO})_6$ (10 mol%), PPh_3 (3 equiv.), 365 nm LED, CPME, 24 h

Ref. 22: $\text{Pt}(\text{+})\text{Cl}(\text{-})$, *n*- Bu_4NBF_4 , $\text{P}(\text{OEt})_3$, HFIP/ $\text{CH}_3\text{CN}/\text{HCOOH}$, N_2 , 10 mA, 3 h

This work:

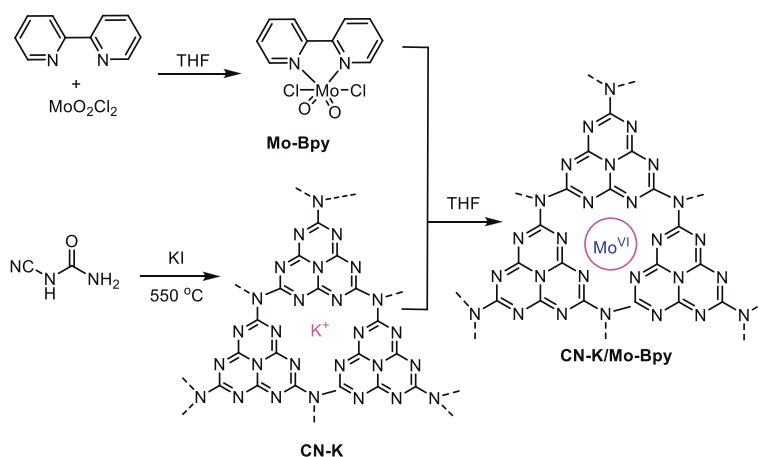
CN-K/Mo-bpy, PPh_3 (2.4 equiv.), ethyl acetate, r.t., 18 h

Scheme 1. Different strategies for synthesis of diarylamines.

the presence of PPh_3 in toluene under N_2 atmosphere at 100°C [19]. Recently, $\alpha\text{-MoO}_3\text{-B}$ and $\text{W}(\text{CO})_6$ -catalyzed, light promoted reaction of aryl boronic acids with nitroarenes was also developed [20,21]. Besides, an electrochemical reductive coupling of nitroarenes and aryl boronic acids was elegantly established by Lei *et al.* [22]. In addition, other innovative methods applying nitroarenes as the direct precursors for P(III)-mediated reductive coupling reaction have also been reported in the past ten years [23–29]. Although remarkable progress has been made, these protocols have their own advantages and some disadvantages, such as the need to provide heat sources, light sources or electrochemical devices, the requirement of ligands, stoichiometric additives and N_2 atmosphere, long reaction time, low product yield and harsh reaction conditions. In addition, most reported methods are homogeneous catalysis, which may lead to complex problems of catalyst recovery, separation, and product purification, resulting in waste of energy and cost, all of which compromise the sustainability of these protocols. Therefore, it is very important to develop a heterogeneous catalyst which can effectively catalyze the amination of boronic acid and nitroarenes under mild conditions (room temperature).

Mesoporous graphite carbon nitride (CN) with covalent conjugate system can be easily obtained by pyrolysis of cheap precursors (including urea, cyanamide or guanidine), which makes their preparation process simple, inexpensive, low toxicity and high thermal/chemical stability [30–37]. Recently, CN acted as a prospective support to stabilize metal catalysts including Ni [38,39], Cu [40,41], Co [42], Ti [43], Ag [44] and Pd [45]. It was also reported that CN can be used as a ligand for direct coordination of metal complex [46,47]. As far as we know, no an example has been disclosed for the amination of boronic acid and nitroarenes using CN supported molybdenum heterogeneous catalytic system. Our group has had a long-standing interest in green organic synthesis, especially heterogeneous catalysis [48–51]. Inspired by the work of Suárez-Pantiga and Sanz's work [17], we designed a new CN-K/Mo-Bpy heterogeneous catalyst by grafting molybdenum complex on $\text{C}_3\text{N}_4\text{-K}$. The CN-K/Mo-Bpy exhibits a high catalytic activity for synthesis of various valuable diarylamines *via* the direct amination of nitroarenes and boronic acid. The method does not need anhydrous solvent or inert atmosphere, and the reaction is completed at room temperature, and no heating equipment is required (Scheme 1).

The synthesizing process of CN-K/Mo-Bpy was shown in Scheme 2. The complex Mo-Bpy was prepared by the standard method of replacing the THF molecules in the solvent adduct $\text{MoO}_2\text{Cl}_2(\text{THF})_2$ by 2,2'-bipyridine ligand. CN-K material was prepared by direct thermal polymerization of dicyandiamide with the addition of potassium iodide [52]. The CN-K/Mo-Bpy catalyst was



Scheme 2. The preparation process of CN-K/Mo-Bpy.

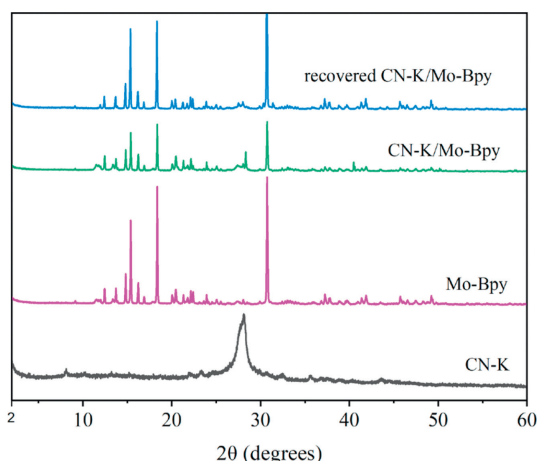


Fig. 2. XRD images of CN-K, Mo-Bpy and CN-K/Mo-Bpy (fresh and recovered).

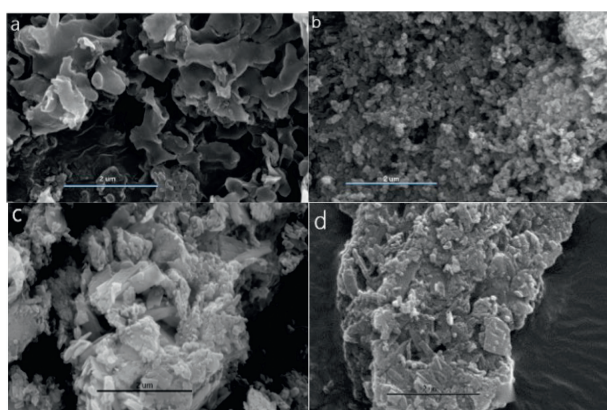


Fig. 3. SEM images of CN-K (a), Mo-Bpy (b) and CN-K/Mo-Bpy (c, fresh) and CN-K/Mo-Bpy (d, recovered).

prepared by cation exchange of K^+ in CN-K by Mo-Bpy in THF for 3 days at room temperature [53].

In order to determine the structure of the designed CN-K/Mo-Bpy, pure CN-K, Mo-Bpy, and CN-K/Mo-Bpy were characterized by X-ray powder diffractometry (XRD). As present in Fig. 2, the pure CN-K has two main diffraction peaks at about 8.0° and 27.8° , corresponding to the repetitive pattern of the in-plane ordering of triazine units and the interlayer stacking reflection of the conjugated aromatic hydrocarbon system with interlayer, respectively. The pure Mo-Bpy has distinct diffraction peaks at 12.4° , 13.7° , 14.8° , 15.4° , 16.29° , 17.0° , 18.3° , 20.0° , 20.6° , 21.4° , 23.9° , 27.3° , 28.3° and 30.7° . No additional peaks corresponding to impurities such as inorganic salts of Mo-Bpy were observed in CN-K/Mo-Bpy. These results show that the ordered structure of the parent CN-K is maintained after immobilization of the Mo complex on the surface.

The morphology of CN-K/Mo-Bpy material was characterized by SEM (Fig. 3). It was observed that pure CN displays an irregular sheet structure. The SEM image of CN-K/Mo-Bpy shows numerous Mo-Bpy dispersed on the CN-K layer. Compared to pure CN-K, the surface morphology of CN-K/Mo-Bpy is rougher and dispersed with numerous particles. The content of Mo in the CN-K/Mo-Bpy catalyst is 17.01%, as determined by inductively coupled plasma optical emission spectrometry (ICP-OES).

The porous properties and specific surface area of CN-K and CN-K/Mo-Bpy were characterized by BET and Barrett-Joyner-Halenda (BJH) methods (Fig. 4). The specific surface area of CN-K/MoO₂Cl₂-

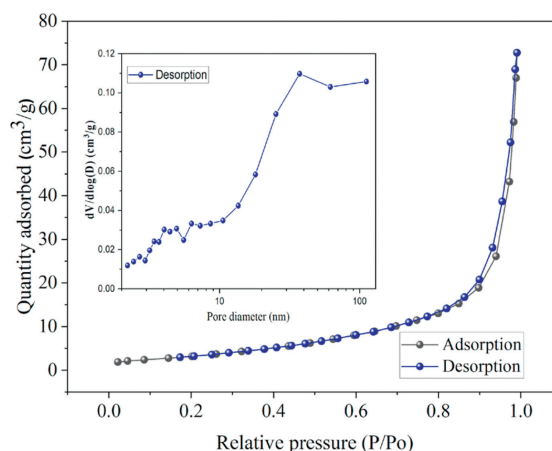


Fig. 4. N₂ adsorption-desorption isotherms of as-prepared CN-K and CN-K/Mo-Bpy.

Bpy was calculated to be $4.70 \text{ cm}^2/\text{g}$, which is slight lower than of CN-K ($5.79 \text{ cm}^2/\text{g}$).

To reveal the chemical states of CN-K/Mo-Bpy catalyst, X-ray photoelectron spectroscopy (XPS) was conducted. The full spectrum of XPS shown in Fig. 5a exhibits that CN-K/Mo-Bpy contains elements C, N, O, Cl and Mo. The N 1s spectra are shown in Fig. 5b, and the main peaks occurred around 399.42 eV and 402.67 eV are assigned to C=N functional group (triazine and pyridinic N), respectively. The presence of Mo⁶⁺ is demonstrated by peaks at 231.64 eV and 234.81 eV (Fig. 5d), which correspond to Mo 3d_{5/2} and Mo 3d_{3/2}, respectively [54]. Compared with Mo-Bpy (Fig. 5c), the binding energy of Mo 3d_{5/2} and Mo 3d_{3/2} in CN-K/Mo-Bpy decreased by 0.81 and 0.86 eV , respectively, suggesting that there may be an interaction between Mo and CN-K in the composite. XPS results further demonstrate the synthesis of CN-K/Mo-Bpy material and there may be interactions between Mo and CN-K.

The FT-IR spectrum of the supported CN-K/Mo-Bpy catalyst (Fig. 6) shows bands characteristic of the CN-K structure, which is dominated by absorptions at 998 cm^{-1} , 1158 cm^{-1} and 2180 cm^{-1} due to C-O vibration and cyano group. In addition, the peaks in the range of $1200\text{--}1600 \text{ cm}^{-1}$ corresponds to the typical tensile vibration of the CN heterocyclic ring. These bands are only slightly shifted compared to those of the unmodified CN-K. The peaks at 1609 and 1591 cm^{-1} may be attributed to the pyridyl stretching vibration of Bpy ligand. In addition, the presence of bands at 901 and 930 cm^{-1} in Mo-Bpy, which can be assigned to the asymmetric and symmetric stretching vibrations of the O=Mo=O group, respectively. After loading CN-K, compared with the stretching vibration of O=Mo=O in CN-K/Mo-Bpy at 903 and 937 cm^{-1} , the peak has a slight red shift, indicating that there is a potential interaction between them. Consistent with the findings of XRD, TEM, SEM, XPS and FT-IR analysis provides further evidence that molybdenum was successfully loaded onto the CN-K.

To investigate the stability and thermal behavior of CN-K/Mo-Bpy, thermogravimetric analysis (TGA) was measured at a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere (Fig. 7). The TGA curve shows that the thermal decomposition temperature of CN-K/Mo-Bpy was around 280°C , which indicates that CN-K/Mo-Bpy has good thermal stability.

Encouraged by the above characterizations, the catalytic activity of CN/MoO₂Cl₂-Bpy was evaluated as a heterogeneous catalyst. For this purpose, model reaction between 1-chloro-4-nitrobenzene and phenylboronic acid was chosen for this amination reaction and selected results are listed in Table 1. As expected, target product **3a** was successfully obtained in 92% yield using CN/MoO₂Cl₂-Bpy as a catalyst, PPh₃ as reductant in ethyl acetate (EA) at room tem-

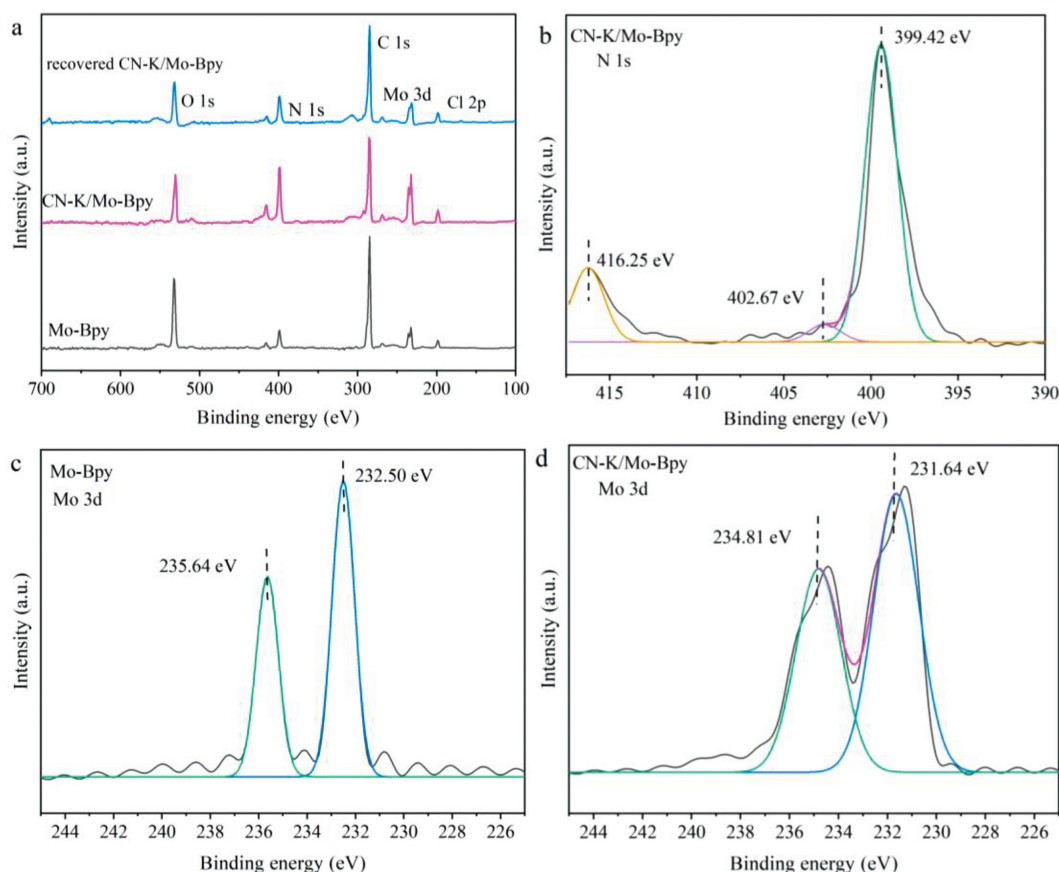


Fig. 5. The XPS spectra of CN-K/Mo-Bpy: wide scan (a), high-resolution spectrum for the N 1s (b), Mo 3d (c, Mo-Bpy) and Mo 3d (d, CN-K/Mo-Bpy).

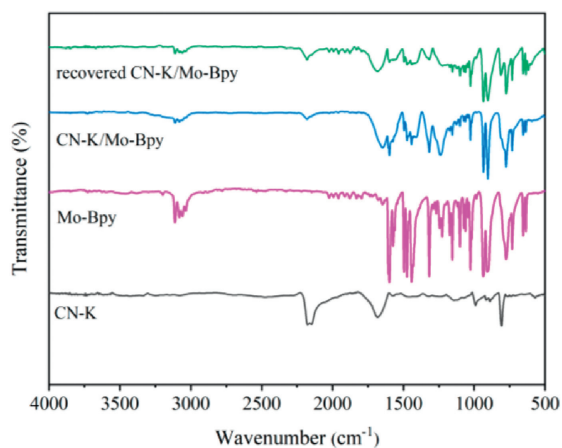


Fig. 6. FT-IR spectra of CN-K, Mo-Bpy and CN-K/Mo-Bpy (fresh and recovered).

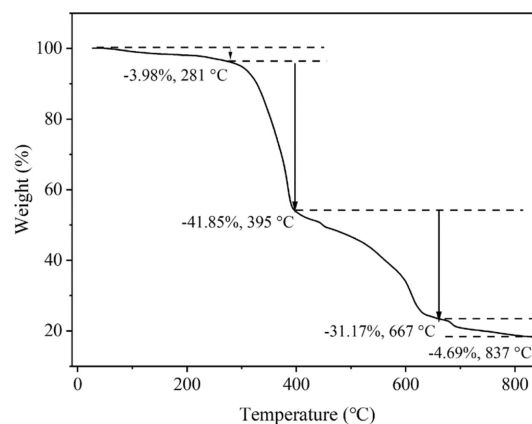
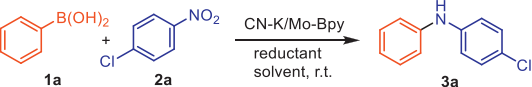


Fig. 7. The TGA patterns of CN-K/Mo-Bpy.

perature for 18 h (Table 1, entry 1). Various conditions were examined with respect to solvent, reductant, the amount of catalyst, and reaction time. First, a series of solvents were investigated in this reaction, and it was found that the solvent had a great influence on the reaction. Only a small amount of product **3a** was observed when the model reaction was carried out in MeOH, EtOH, 1,4-dioxane, DMF, DMSO, ethyl lactate (EL), and γ -valerolactone (GVL). When the reaction was carried out in toluene, cyclopentyl methyl ether (CPME), 2-methyltetrahydrofuran (2-Me-THF), CH₃CN, and dichloromethane (DCM), **3a** was obtained in 28%–88% yield (Table 1, entries 2–13). Dimethyl carbonate (DMC) was found out to be the optimal solvent and produced **3a** was obtained in 90%

yield (entry 14). Considering the reaction yield, availability, cost and environmental factors, ethyl acetate (EA) was selected as an optimal solvent. Next, some reductants were also screened and it was found that more conventional reductants such as Cu, Zn, NaBH₄, FeCl₂, SnCl₂, Na₂SO₃, Na₂S, triethylsilane, phenylsilane and hydrazine hydrate are ineffective for the reaction (entries 15–24). The replacement of PPh₃ with tributylphosphine (P^tBu₃), diethyl phosphite, and diphenyl phosphite as the reducing agent led to a dramatic decrease of yield (entries 25–27). The amount of PPh₃ played an important role in this reaction. Only 65% of the desired product was obtained when 1.0 equiv. of PPh₃ was used (entry 28). Reducing the amount of PPh₃ to 2.0 equiv. decreased the yield of **3a** to 84% (entry 29). In addition, increasing PPh₃ from 2.4 equiv.

Table 1
Optimization of the reaction condition for synthesis of **3a**.^a



Entry	Solvent	Reductant	Time (h)	Yield (%) ^b
1	EA	PPh ₃	18.0	92
2	MeOH	PPh ₃	18.0	trace
3	EtOH	PPh ₃	18.0	trace
4	1,4-Dioxane	PPh ₃	18.0	trace
5	DMF	PPh ₃	18.0	trace
6	DMSO	PPh ₃	18.0	trace
7	EL	PPh ₃	18.0	trace
8	GVL	PPh ₃	18.0	trace
9	Toluene	PPh ₃	18.0	28
10	CPME	PPh ₃	18.0	58
11	2-Me-THF	PPh ₃	18.0	60
12	CH ₃ CN	PPh ₃	18.0	68
13	DCM	PPh ₃	18.0	88
14	DMC	PPh ₃	18.0	90
15	EA	Cu	18.0	trace
16	EA	Zn	18.0	trace
17	EA	NaBH ₄	18.0	trace
18	EA	FeCl ₂	18.0	trace
19	EA	SnCl ₂	18.0	trace
20	EA	Na ₂ SO ₃	18.0	trace
21	EA	Na ₂ S	18.0	trace
22	EA	Triethylsilane	18.0	trace
23	EA	Phenylsilane	18.0	trace
24	EA	hydrazine hydrate	18.0	trace
25	EA	P ^t Bu ₃	18.0	38
26	EA	(EtO) ₂ P(O)H	18.0	45
27	EA	(PhO) ₂ P(O)H	18.0	68
28 ^c	EA	PPh ₃	18.0	65
29 ^d	EA	PPh ₃	18.0	84
30 ^e	EA	PPh ₃	18.0	92
31 ^f	EA	PPh ₃	18.0	85
32 ^g	EA	PPh ₃	18.0	92
33	EA	PPh ₃	10.0	78
34	EA	PPh ₃	14.0	86
35	EA	PPh ₃	20.0	92
36 ^h	EA	PPh ₃	18.0	88
37 ⁱ	EA	PPh ₃	18.0	82
38 ^j	EA	PPh ₃	18.0	trace
39 ^k	EA	PPh ₃	18.0	75
40 ^l	EA	PPh ₃	18.0	85

^a Reaction condition: 1-chloro-4-nitrobenzene (1.0 mmol), phenylboronic acid (1.5 mmol), catalyst (40 mg), reductant (2.4 mmol) in solvent (3 mL), room temperature, air.

^b Isolated yield based on **2a**.

^c PPh₃ (1.0 mmol).

^d PPh₃ (2.0 mmol).

^e PPh₃ (3.0 mmol).

^f CN-K/Mo-Bpy (30 mg).

^g CN-K/Mo-Bpy (50 mg).

^h Phenylboronic acid (1.2 mmol).

ⁱ Phenylboronic acid (1.0 mmol).

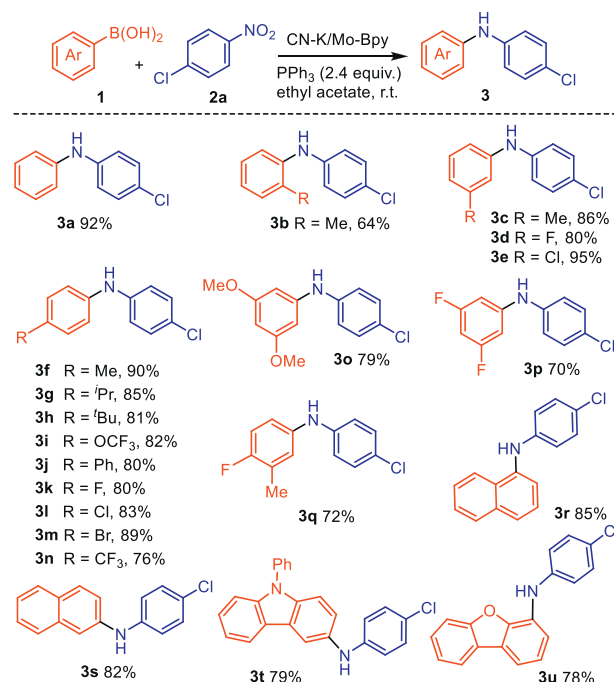
^j Pure CN-K was used.

^k Pure Mo-Bpy was used.

^l Mo-Bpy and CN-K were used.

to 3.0 equiv. did not further increase the yield (entry 30). Further screening of other reaction parameters such as the amount of catalyst and the ratio of the reactants as well as reaction time failed to improve the yield of **3a**.

Notably, when pure CN-K was used as the catalyst, the target product **3a** was not observed. The use of homogeneous Mo-Bpy resulted in a low conversion into the desired product **3a**. For further comparison, the combination of CN-K and Mo-Bpy was examined, and it was found that the catalytic activity was poor compared with CN-K (entries 38–40). The result reveals that the well dispersed Mo-Bpy interacted with CN afford an open reaction microenvironment, which can make the catalyst better contact with

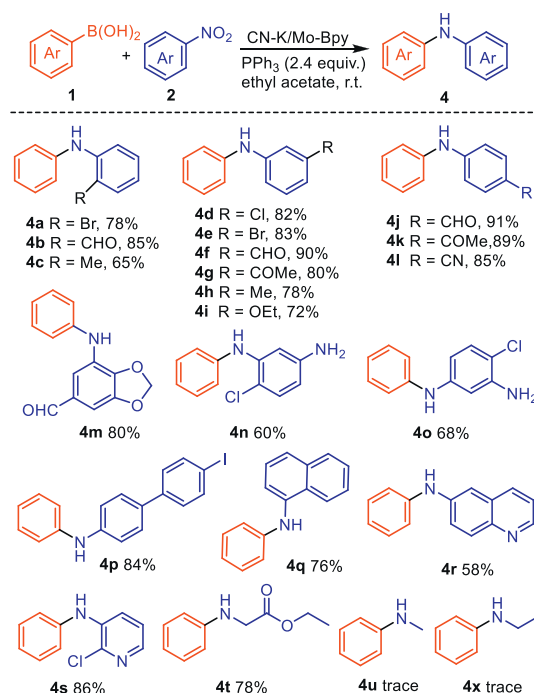


Scheme 3. Substrate scope for (hetero)aryl boronic acids. Reaction conditions: nitroarene (1.0 mmol), arylboronic acid (1.5 mmol), PPh₃ (2.4 mmol), CN-K/Mo-Bpy (40 mg), ethyl acetate (3 mL) at room temperature for 18 h, isolated yields based on **2**.

reactant molecules, thus improving the reactivity. Therefore, the optimum reaction conditions as shown in entry 1, successfully provide **3a** in a heterogeneous catalytic manner with 92% yield.

The optimized reaction conditions were established, the substrate scope was evaluated. First, we turned our attention to the generality of arylboronic acid. As presented in Scheme 3, a plethora of different phenylboronic acid with different substituents (including electron-withdrawing and electron-donating groups) at the *para*, *meta* and *ortho* positions of benzene ring reacted smoothly with 1-chloro-4-nitrobenzene to furnish the target products (**3a–3m**) in good to high yields. Satisfactory, the arylboronic acid containing a strong electron-withdrawing CF₃ group on the benzene ring delivered the desired product **3n** with a yield of 76%. Meanwhile, the substrates with polysubstituted groups in the phenyl ring of arylboronic acid worked smoothly as well. Notably, polycyclic boronic acid such as naphthalen-1-ylboronic acid, and naphthalen-2-ylboronic acid were also eligible substrates for this reaction to afford the expected product in high yield. Additionally, this protocol was applicable to hetero-aryl boronic acids, such as dibenzo[*b,d*]furan-4-ylboronic acid and (9-phenyl-9H-carbazol-1-yl)boronic acid, and the desired product **3t** and **3u** were generated in high yield.

Thereafter, we continued to explore the substrate scope by varying the structure of nitroarene under the established optimal reaction conditions and the results are summarized in Scheme 4. As expected, a wide range of nitroarene possessing different functional groups on the benzene ring, such as Me, OEt, or COMe, were well tolerated, and the corresponding arylidiphenylamines were isolated in good to high yields. Moreover, a variety of substituents on different positions of the benzene ring of the nitroarene were interrogated. It is noted that nitroaromatics with substituents in *ortho* position successfully delivered the desired products, which reveals the good adaptability of the protocol to the steric hindrance of the substrate. It's also worth mentioning that halogen substituents remained unchanged under the applied reaction conditions, thus providing convenient synthetic handles for further



Scheme 4. Substrate scope with nitroarenes. Reaction conditions: nitroarene (1.0 mmol), phenylboronic acid (1.5 mmol), PPh₃ (2.4 mmol), CN-K/Mo-Bpy (40 mg), ethyl acetate (3 mL) at room temperature for 18 h, isolated yields based on **2**.

structural elaboration. Although this is a reduction process, ketones and even aldehydes will not be reduced, which is contrary to the classical reductive amination, which needs to protect these functional groups. It is particularly noteworthy that when free amine also exists, amination selectively occurs on nitro groups, while amino groups do not need protection. This example clearly shows that the reaction is not carried out through amino groups. Likewise, polycyclic nitroarenes reacted smoothly to produce the corresponding products in high yield. Interestingly, 4-iodo-4'-nitro-1,1'-biphenyl including -I group on the phenyl ring was found to be well-tolerated under the optimized conditions, giving the corresponding product **4p** in 84% yield. Of note, the performance is accomplished with nitroarenes containing several medically relevant nitrogen-containing heterocycles such as quinoline and pyridine, albeit with somewhat diminished yields. Remarkably, the process has also revealed to be compatible with ethyl nitroacetate and gave desired product **4t** with 78% yield. Unfortunately, when nitroalkanes such as nitromethane and nitroethane are used as substrates, it is found that low conversion was achieved and only a small amount of desired alkylated aniline was detected.

The late-stage modification of bioactive molecules has become a powerful and effective tool for quickly discovering new drug candidates. To showcase the applicability of the present method to late-stage synthesis, a variety of bioactive molecules were surveyed (Scheme 5). For example, DL-menthol (**5**), cholesterol (**9**), and dehydroabietylamine (**12**) reacted with 4-nitrobenzoyl chloride (**6**) to give intermediates **7**, **10** and **13**, respectively, which were reacted with 4-methyl phenylboronic acid under standard conditions to provide the target products **8**, **11** and **14** in 72%, 71% and 78% yields.

Another synthetic utility of our protocol is the synthesis of mefenamic acid, a non-steroidal anti-inflammatory drug. It could be obtained by the reaction of 2-cyanonitrobenzene (**15**) with 2,3-dimethylphenylboronic acid (**16**) after hydrolysis of the cyano group, with an overall yield of 59% (Scheme 6a). Collectively, this method demonstrated the potential utility of synthesizing drug-

related compounds. In addition, the reaction protocol was amendable to a preparative scale synthesis. The model reaction based on 10 mmol of 1-chloro-4-nitrobenzene was carried out under the standard condition, giving the desired product **3a** in an amount of 1.83 g (90% yield) (Scheme 6b).

Several control experiments were performed to gain insight into the mechanism (Scheme 7). When the model reaction was performed in dry ethyl acetate under an inert atmosphere, it was found that only a trace amount of desired product **3a** was detected. Meanwhile, when deuterated water was added, deuterated product **3a'** was formed. These results indicated that water is crucial for the success of this transformation. The water involved in the reaction may come from solvent or air. In addition, nitroso compound was detected in reaction mixture by HRMS during the reaction process. Additionally, **3a** can be rapidly generated when **1a** was replaced by 1-chloro-4-nitrosobenzene, which suggested that the formation of nitroso compound may be the rate-determining step.

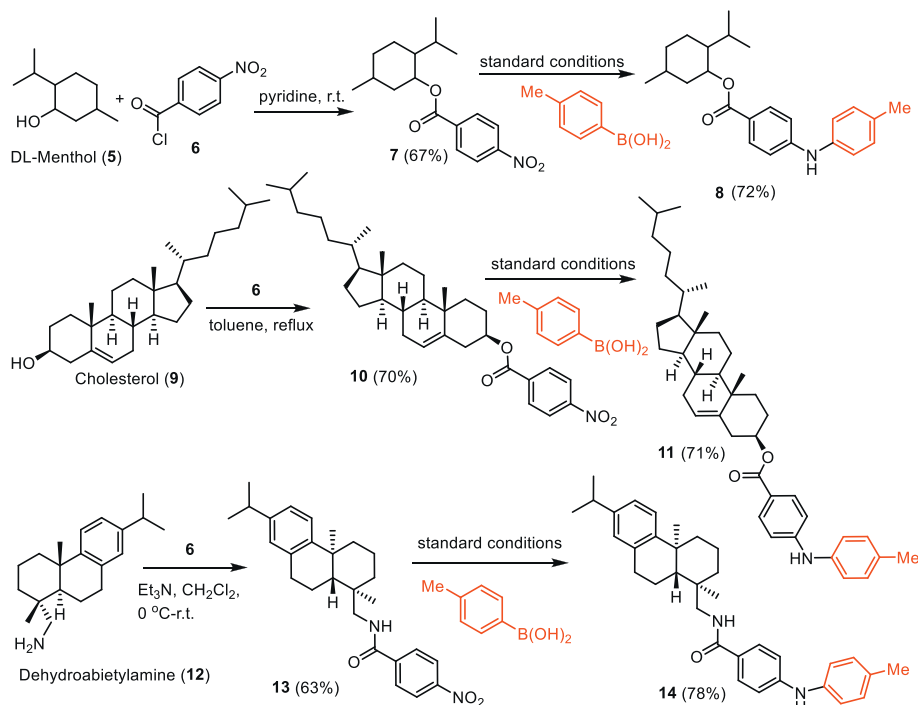
On the basis of presented above and precedent reports [17,19], a tentative reaction mechanism for direct amination of nitro compound with arylboronic acid is outlined in Scheme 8. As is known, molybdenum(VI) can be easily reduced by PPh₃ to generate Mo(IV), which can coordinate with nitro compound to provide intermediate **I**. Next, the re-oxidation of Mo center by coordinated nitroarenes produces intermediate **II** with nitroso ligand. Intermediate **II** releases free nitroso compound **III**, accompanied by the regeneration of the original catalyst. Subsequently, nitroso compound **III** interacted both with Ar²B(OH)₂ and PPh₃ to afford nitrenoid borate intermediate **IV**. Later, 1,2-migration of a nucleophilic Ar² group to adjacent N center and spontaneous release of O=PPh₃ leads to the formation of the aminoboronic acid **V**. Finally, a diarylamine product was obtained by hydrolysis.

To further illustrate the practicability of this heterogeneous catalyzed protocols, a recycling procedure was established. The CN-K/Mo-Bpy was recovered after each reaction by centrifugation, washed, and subsequently reused in the next cycles. As shown in Fig. 8, the recovered CN-K/Mo-Bpy can be reused five times for the model reaction without the loss of its catalytic reactivity. The PXRD, SEM, and FTIR results (Figs. 2, 3 and 6) of the catalyst were not significantly different from the original CN-K/Mo-Bpy after five cycles. The results confirmed the good stability of the CN-K/Mo-Bpy under current conditions.

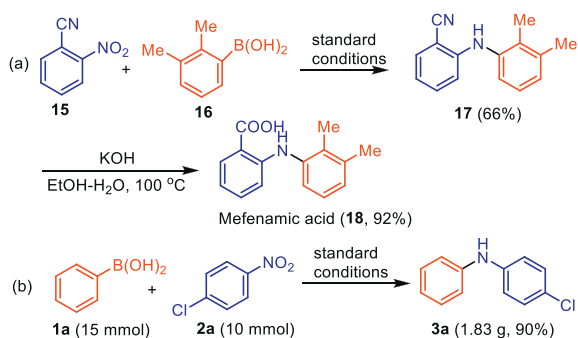
In conclusion, a heterogeneous catalyst (CN-K/Mo-Bpy) employing Mo anchored on C₃N₄ with 2,2'-bipyridine ligand was developed and characterized. The designed CN-K/Mo-Bpy exhibits high catalytic activity with the use of affordable PPh₃ as reductant for synthesis of (hetero)aryl amines from commercially available nitroarenes in a single synthetic operation. This protocol is rather practical as no special equipment is required, and ambient temperature is sufficient to achieve high to excellent yield of the secondary aromatic amines with wide substrate scope and excellent functional-group compatibility. Additionally, the potential of our method is further demonstrated by the late-stage modifications of bioactive molecules and the gram scale synthesis. The heterogeneous nature of the reaction system enables the catalyst to be recovered and reused for five times without obvious loss of its catalytic activity. Continuous research on organic synthesis using heterogeneous catalysts in our group is ongoing and will be reported in due course.

Declaration of competing interest

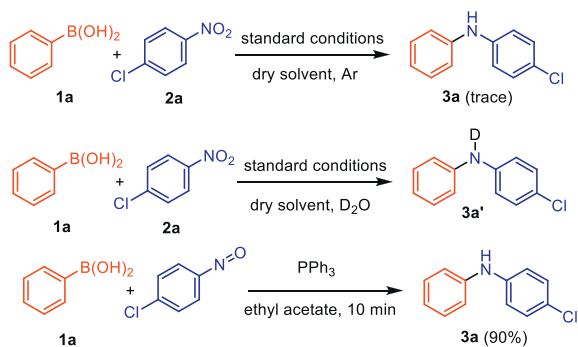
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.



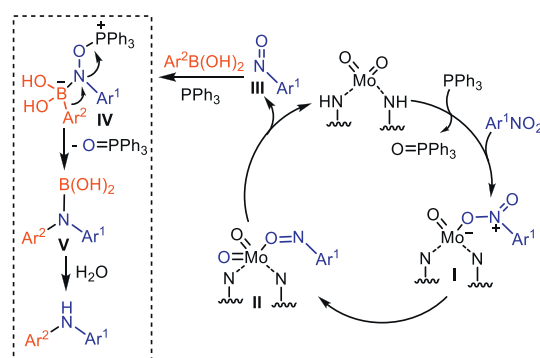
Scheme 5. Late-stage modification.



Scheme 6. Synthetic application and gram-scale synthesis.



Scheme 7. Control experiments.



Scheme 8. Proposed mechanism for direct amination of nitroarene with arylboronic acid.

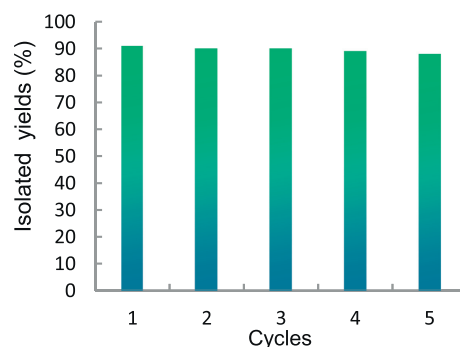


Fig. 8. Stability and recycling of CN-K/Mo-Bpy for the synthesis of 3a.

CRediT authorship contribution statement

Wen-Jing Li: Data curation, Conceptualization. **Jun-Bo Wang:** Methodology, Data curation. **Yu-Heng Liu:** Funding acquisition, Conceptualization. **Mo Zhang:** Writing – original draft, Funding acquisition. **Zhan-Hui Zhang:** Writing – review & editing, Project administration, Funding acquisition, Conceptualization.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ccl.2024.110001.

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